

The VSEPR Theory of Molecular Geometry

VSEPR stands for Valence Shell Electron Pair Repulsion. That's a real mouthful for what is really a rather simple idea.

The whole concept revolves around the idea that the electrons in a molecule repel each other and will try and get as far away from each other as possible. VSEPR explains a lot about molecular geometry and structure, BUT NOT EVERYTHING!!

The electrons (both in pairs and singles as you will see) are "attached" to a central atom in the molecule and can "pivot" freely on the atom's surface to move away from the other electrons.

Electrons will come in several flavors:

- a) bonding pairs - this set of two electrons is involved in a bond, so we will write the two dots BETWEEN two atoms. This applies to single, double, and triple bonds.
- b) nonbonding pairs - this should be rather obvious.
- c) single electrons - in almost every case, this single electron will be nonbonding.

Almost 100% of the examples will involve pairs, but there are a significant number of examples that involve a lone electron.

VSEPR uses a set of letters to represent general formulas of compounds. These are:

- a) A - this is the central atom of the molecule (or portion of a large molecule being focused on).
- b) X - this letter represents the ligands or atoms attached to the central atom. No distinction is made between atoms of different elements. For example, AX_4 can refer to CH_4 or to CCl_4 .
- c) E - this stands for nonbonding electron pairs.
- d) e - this stands for lone nonbonding electrons.

Each area where electrons exist is called an "electron domain" or simply "domain." It does not matter how many electrons are present, from one to six, it is still just one domain. Now a domain with six electrons in it (a triple bond) is bigger (and more repulsive) than a lone-electron domain. However, it is still just one domain.

This is an IMPORTANT point to remember in VSEPR. The more electrons in a domain, the more repulsive it is and it will push other domains farther away than if all domains were equal in strength. Keep in mind that the domains are all attached to the central atom and will pivot so as to maximize the distance between domains.

Another important point to mention in this introduction is that an element's electronegativity will play an important role in determining its role in the molecule.

For example, the least electronegative element will be the central atom in the molecule. The more electronegative the element, the more attractive it is to its bonding electrons. This will play a very important role, especially in five domains.

The most important domain numbers at the introductory level are 3, 4, 5, and 6. Domains of 1 and 2 exist, but are simple to figure out. We'll do them here in the ChemTeam. Domains up to 9 exist, but become progressively more complex. If you decide you **MUST** study those domains, seek out this book:

The VSEPR Model of Molecular Geometry (1991) by Ronald J. Gillespie and István Hargittai. Published by Allyn & Bacon. ISBN 0-205-12369-4.

Gillespie coined the term VSEPR and has been active in this field since it was established in the early 1940's. Except where noted, all bond angles and bond lengths have been taken from this book.

Table of Three to Six Electron Domains

Number of Domains	Arrangement of Domains	General Molecular Formula	Molecular Shape	Examples
3	Equilateral triangular (three domains)	AX_3	Trigonal planar	BCl_3 , $AlCl_3$
		AX_2E	Angular	$SnCl_2$
4	Tetrahedral (four domains)	AX_4	Tetrahedral	CH_4 , $SiCl_4$
		AX_3E	Trigonal pyramidal	NH_3 , PCl_3
		AX_2E_2	Angular	H_2O , SCl_2
5	Trigonal bipyramidal (five domains)	AX_5	Trigonal bipyramidal	PCl_5 , AsF_5
		AX_4E	Disphenoidal	SF_4
		AX_3E_2	T-shaped	ClF_3
		AX_2E_3	Linear	XeF_2
6	Octahedral (six domains)	AX_6	Octahedral	SF_6
		AX_5E	Square pyramidal	BrF_5
		AX_4E_2	Square planar	XeF_4

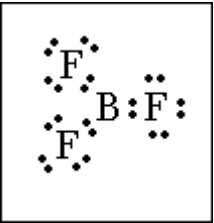
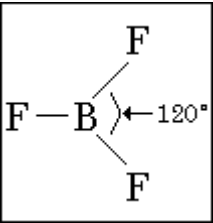
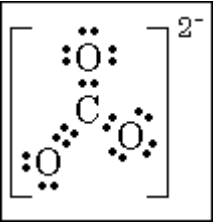
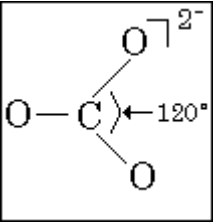
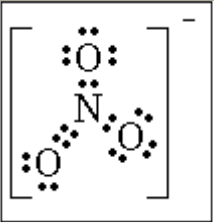
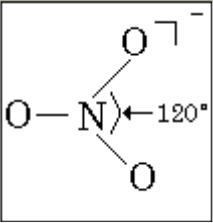
Three Electron Domains

Three electron domains around a central atom is known generally as trigonal planar (sometimes triangular planar) and has two major variations you should know:

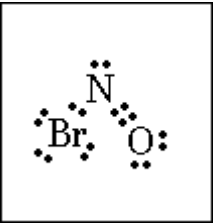
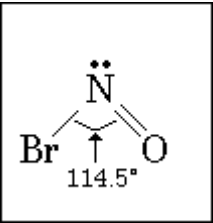
AX₃ - trigonal planar

AX₂E - angular

AX₃ - Trigonal planar

Molecule	Lewis Structure	3-D Structure	Comments
BF ₃			Note that BF ₃ is electron-deficient, with only six electrons in boron's valence shell. This will make it a good Lewis acid. BH ₃ does not exist as an independent species, but B₂H₆ (named diborane) does.
CO ₃ ²⁻			Formal charge places a -1 on each of the oxygens with three electron pairs. This ion shows resonance structures. All three bond lengths are equal and intermediate between a C-C bond (134 pm) and a C=C bond (154 pm) at about 147 pm.
NO ₃ ⁻			Formal charge places a -1 on the oxygens with three electron pairs and a +1 on the N. This ion shows resonance structures. All three bond lengths are equal and intermediate between a N-O bond (136 pm) and a N=O bond (116 pm) at about 130 pm.

AX₂E - Angular

Molecule	Lewis Structure	3-D Structure	Comments
BrNO			CINO has a bond angle of 113.3° and FNO has a bond angle of 110.1°. Can you explain why? Hint: think about what the increasing electronegativity of Br to Cl to F does to the electron density (hence repulsive power) of that bonding domain.

Four Electron Domains

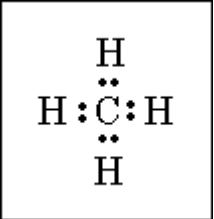
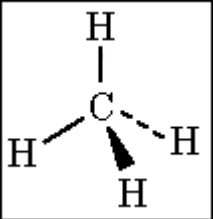
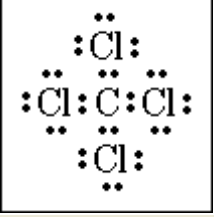
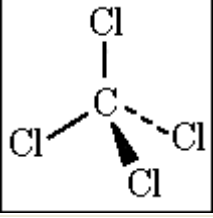
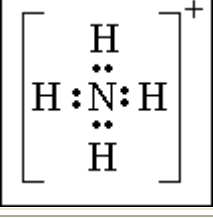
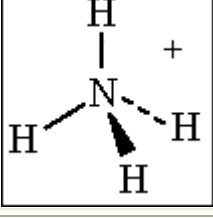
Four electron domains around a central atom is known generally as tetrahedral and has three major variations you should know:

AX_4 - tetrahedral

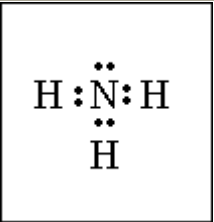
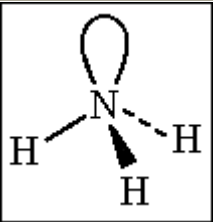
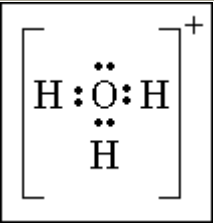
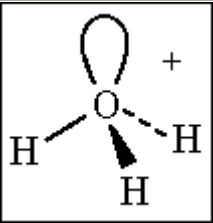
AX_3E - trigonal pyramidal

AX_2E_2 - angular

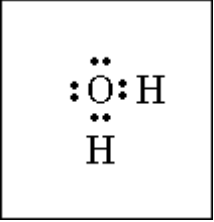
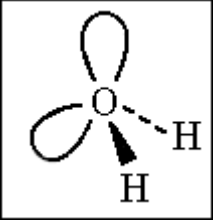
AX_4 - Tetrahedral

Molecule	Lewis Structure	3-D Structure	Comments
CH_4			<p>The H-C-H angle is the classic tetrahedral angle of 109.5°</p> <p>A very interesting result of molecular orbital theory is that CH_4 has one bond different than the other three.</p>
CCl_4			tetrahedral
NH_4^+			tetrahedral

AX₃E - Trigonal pyramidal

Molecule	Lewis Structure	3-D Structure	Comments
NH ₃			<p>Since the nonbonding pair is larger (and more repulsive) than a bonding pair, the hydrogens are pushed together and the H-N-H bond angle is 107.2°. The bond angle in NF₃ is 102.3° due to the greater electronegativity of F.</p>
H ₃ O ⁺			<p>The H-O-H bond angle varies depending on the presence of other ions in the solid.</p>

AX₂E₂ - Angular

Molecule	Lewis Structure	3-D Structure	Comments
H ₂ O			<p>The H-O-H bond angle is 104.5°</p>

Five Electron Domains

Five electron domains around a central atom is known generally as trigonal bipyramidal and has four major variations you should know:

AX_5 - trigonal bipyramid

AX_4E - disphenoidal

AX_3E_2 - T-shaped

AX_2E_3 - linear

AX_5 - Trigonal bipyramid

Molecule	Lewis Structure	3-D Structure	Comments
PF_5			trigonal bipyramid
OSF_4			The color red is simply there to help tell the electron pairs apart. It serves no other function.

AX_4E - Disphenoidal

Molecule	Lewis Structure	3-D Structure	Comments
SF_4			disphenoidal: the unshared electron pair is in the plane of the page. Also called see-saw or teeter-totter.

AX₃E₂ - T-shaped

Molecule	Lewis Structure	3-D Structure	Comments
ClF ₃			T-shaped: the two unshared electron pairs are projected in front of and behind the plane of the page.

AX₂E₃ - Linear

Molecule	Lewis Structure	3-D Structure	Comments
I ₃ ⁻			linear

Six Electron Domains

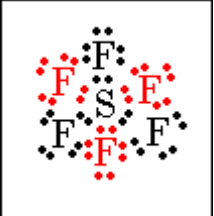
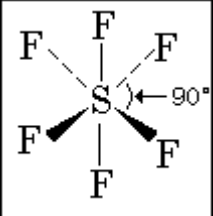
Six electron domains around a central atom is known generally as octahedral and has three major variations you should know:

AX_6 - octahedral


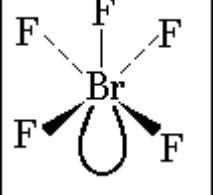
AX_5E - square pyramidal

AX_4E_2 - square planar

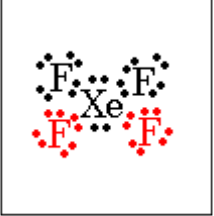
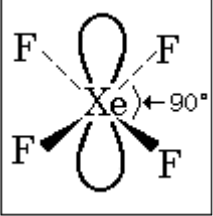
AX_6 - Octahedral

Molecule	Lewis Structure	3-D Structure	Comments
SF_6			octahedral

AX_5E - Square pyramidal

Molecule	Lewis Structure	3-D Structure	Comments
BrF_5			square pyramidal

AX_4E_2 - Square planar

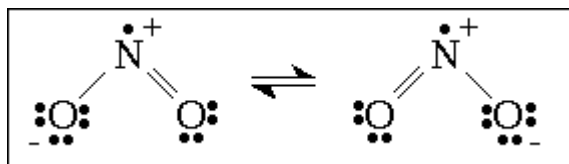
Molecule	Lewis Structure	3-D Structure	Comments
XeF_4			square planar

VSEPR Structures of Odd Electron Molecules

All the usual rules of building a VSEPR structure will apply - minimize formal charge, build octet on more electronegative ligand first, etc.

Example Number One - nitrogen dioxide NO_2

This molecule has a total of 17 electrons to place - five from the nitrogen and 12 from the oxygens. I will go immediately to the final structure:



Notice that I show both [resonance structures](#). Since there are three electron domains, this is a trigonal planar arrangement, but it is signified AX_2e , to signal the single electron domain, also called a half-filled orbital.

The bond angles are not 120° , since the repulsive power of the single electron is less than if there were two. So, the O-N-O bond angle moves outward to 134.3° . Adding another electron to make NO_2^- (which creates a full non-bonding electron pair, changes the O-N-O angle to 115.4° and removing an electron (to make NO_2^+) creates an O-N-O bond angle of 180° .

Example Number Two - chlorine dioxide ClO_2

The substance has 19 electrons to place and is a tetrahedral family member. Its geometry can be described as AX_2Ee . It will have a non-bonding pair and a non-bonding single electron.

Your assignment is to draw this structure. One hint: if you draw it singly bonding, you will arrive at a structure with a formal charge of +2 on the Cl and -1 on each oxygen. Draw a structure to remove those; the correct structure having no formal charge separation whatsoever.

The O-Cl-O bond angle in ClO_2 is 118° . You may wish to ponder the effect on the bond angle in ClO_2^+ and ClO_2^- .

RULES FOR LEWIS STRUCTURES

A Lewis structure consists of the electron distribution in a compound and the formal charge on each atom. You are expected to be able to draw such structures to represent the electronic structure of compounds. The following rules are given to assist you.

1. Determine whether the compound is covalent or ionic. If covalent, treat the entire molecule. If ionic, treat each ion separately. Compounds of low electronegativity metals with high electronegativity nonmetals ($\Delta\text{EN} > 1.6$) are ionic as are compounds of metals with polyatomic anions. For a monoatomic ion, the electronic configuration of the ion represents the correct Lewis structure. For compounds containing complex ions, you must learn to recognize the formulas of cations and anions.

2. Determine the total number of valence electrons available to the molecule or ion by:

(a) summing the valence electrons of all the atoms in the unit and
(b) adding one electron for each net negative charge or subtracting one electron for each net positive charge. Then divide the total number of available electrons by 2 to obtain the number of electron pairs (E.P.) available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.

4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) in the following manner until all available pairs have been distributed:

- a) One pair between the central atom and each ligand atom.
- b) Three more pairs on each outer atom (except hydrogen, which has no additional pairs), yielding 4 E.P. (i.e., an octet) around each ligand atom when the bonding pair is included in the count.
- c) Remaining electron pairs (if any) on the central atom.

5. Calculate the formal charge (F) on the central atom.

- a) Count the electrons shared as bonds. Total = b
- b) Count the electrons owned as lone pairs. Total = n
- c) $F = V - (n + b/2)$, where V = number of valence electrons for the atom.

6. If the central atom formal charge is zero or is equal to the charge on the species, the provisional electron distribution from (4) is correct. Calculate the formal charge of the ligand atoms to complete the Lewis structure.

7. If the structure is not correct, calculate the formal charge on each of the ligand atoms. Then to obtain the correct structure, form a multiple bond by sharing an electron pair from the ligand atom that has the most negative formal charge.

- a) For a central atom from the second ($n = 2$) row of the periodic table continue this process sequentially until the central atom has 4 E.P. (an octet).
- b) For all other elements, continue this process sequentially until the formal charge on the central atom is reduced to zero or two double bonds are formed.

8. Recalculate the formal charge of each atom to complete the Lewis structure. Written by Patrick A. Wegner; California State University, Fullerton.

Writing Lewis Structures: Obeying The Octet Rule

A Lewis structure consists of the electron distribution in a compound and the formal charge on each atom. You are expected to be able to draw such structures to represent the electronic structure of compounds. The following examples will be guided by the previous set of rules.

All these examples obey the octet rule: eight electrons in the valence shell is stable.

Example #1 - Methane CH_4

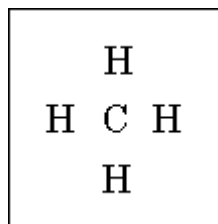
- 1. This compound is covalent.
- 2. Determine the total number of valence electrons available:

One carbon has 4 valence electrons

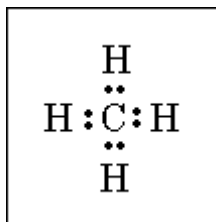
Four hydrogen, each with one valence electron, totals 4

This means there are 8 valence electrons, making 4 pairs, available.

- 3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The structure in step 4 is the correct answer.

Example #2 - Ammonia NH_3

1. This compound is covalent.

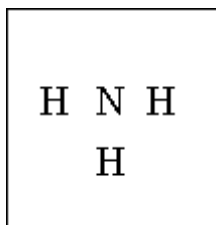
2. Determine the total number of valence electrons available:

One nitrogen has 5 valence electrons

Three hydrogen, each with one valence electron, totals 3

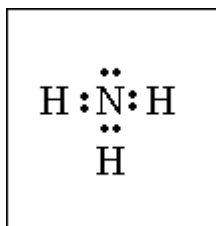
This means there are 8 valence electrons, making 4 pairs, available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



It does not matter which of the three sides you use to put hydrogens on.

4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The structure in step 4 is the correct answer.

Example #3 - Water H₂O

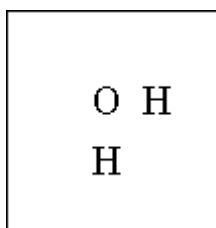
1. This compound is covalent.
2. Determine the total number of valence electrons available:

One oxygen has 6 valence electrons

Two hydrogen, each with one valence electron, totals 2

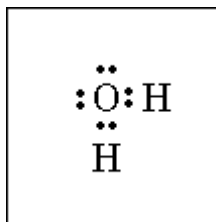
This means there are 8 valence electrons, making 4 pairs, available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



It does matter which of the two sides you use to put hydrogens on. Use sides that are next to each other. DO NOT put the hydrogens 180 degrees apart. There is a reason for this you'll learn later.

4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The structure in step 4 is the correct answer.

Example #4 - Carbon tetrachloride CCl_4

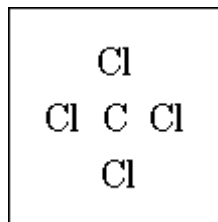
1. This compound is covalent.
2. Determine the total number of valence electrons available:

One carbon has 4 valence electrons

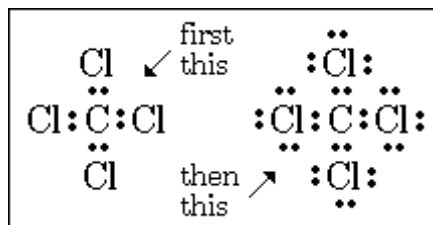
Four chlorine, each with 7 valence electrons, totals 28

This means there are 32 valence electrons, making 16 pairs, available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The structure in step 4 is the correct answer.

Writing Lewis Structures: Expanded and Deficient Octets

A Lewis structure consists of the electron distribution in a compound and the formal charge on each atom. You are expected to be able to draw such structures to represent the electronic structure of compounds. The following examples will be guided by a set of rules. You might want to examine the steps listed under number 4 of the rules.

All these examples will violate the octet rule: more than eight electrons in the valence shell is stable. Six electrons is a bit of a different story. It will come at the end of the file. Also, all these examples have single bonds only. Multiple bonds will come later.

Example #1 - SF₄

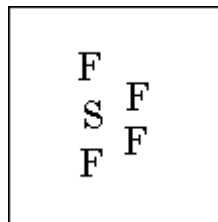
1. This compound is covalent.
2. Determine the total number of valence electrons available:

One sulfur has 6 valence electrons

Four fluorine, each with 7 valence electron, totals 28

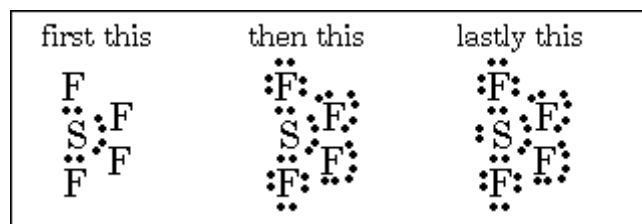
This means there are 34 valence electrons, making 17 pairs, available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



I put the fluorines like I did because I knew I needed an open space for the unbonded pair on the sulfur. If you put the 4 fluorines around the S like in CH₄, that's OK. It gets tiresome making all this little graphic files, but hey, I knew that when I took on this project. OK, enough complaining, back to work.

4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The right-hand structure in step 4 is the correct answer.

Example #2 - ClF_3

1. This compound is covalent.

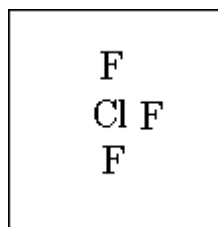
2. Determine the total number of valence electrons available:

One chlorine has 7 valence electrons

Three fluorine, each with 7 valence electron, totals 21

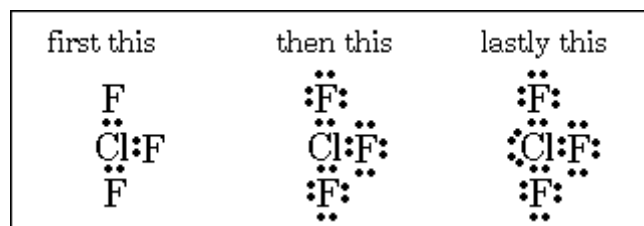
This means there are 28 valence electrons, making 14 pairs, available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



It does not matter which of the three sides you use to put hydrogens on.

4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The structure in step 4 is the correct answer.

Example #3 - I_3^-

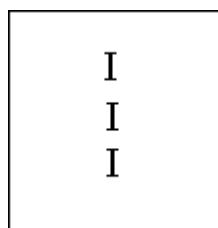
1. This compound is covalent.
2. Determine the total number of valence electrons available:

Three iodine, each with 7 valence electrons, has 21 valence electrons

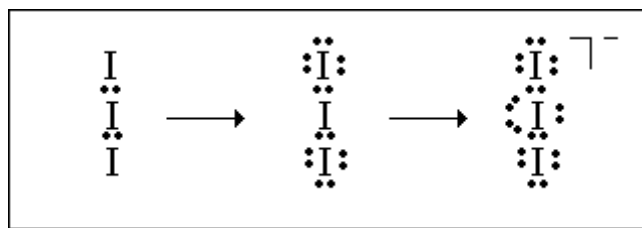
One additional negative charge gives 1

This means there are 22 valence electrons, making 11 pairs, available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The right-hand structure in step 4 is the correct answer.

Please note that the iodines are in a straight line. If you placed them at 90 degrees, then this is incorrect. There is a reason for this and it is discussed in the VSEPR section.

Example #4 - XeF₄

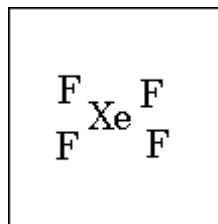
1. This compound is covalent.
2. Determine the total number of valence electrons available:

One xenon has 8 valence electrons

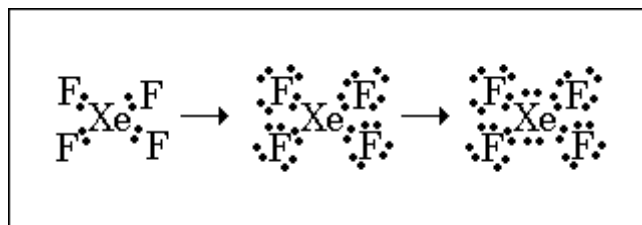
Four fluorine, each with 7 valence electrons, totals 28

This means there are 36 valence electrons, making 18 pairs, available.

3. Organize the atoms so there is a central atom (usually the least electronegative) surrounded by ligand (outer) atoms. Hydrogen is never the central atom.



4. Determine a provisional electron distribution by arranging the electron pairs (E.P.) until all available pairs have been distributed:



5. The formal charge (F) on the central atom is zero. The structure in step 4 is the correct answer.

Prediction of Molecular Polarity for Simple Chemical Species

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The general principle in predicting molecular polarity is the comparison of similar regions of the molecule.

I. If all similar regions are not the same, the chemical species is polar unless symmetry takes precedence. A general idea of the polarity direction (towards the negative region) may be obtained from electronegativity values and/or formal charge.

II. If all similar regions are the same, the chemical species is nonpolar.

It is important to draw a distinction between bond polarity (as determined by electronegativity differences) and molecular polarity (as determined by the shape of the molecule). It is unfortunate that the same words (polar and nonpolar) have been used in both situations.

Designation of Similar Regions by Geometry

Taking into Account Lone Pairs and/or Single Unpaired Electrons

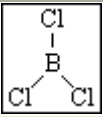
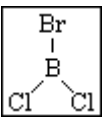
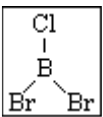
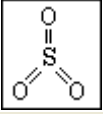
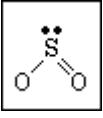
You must be able to construct a correct Lewis structure for a given molecule in order to determine its geometry.

Geometry	Similar Regions
Linear	Ends
Trigonal Planar	Corners of the triangle
Tetrahedral	corners of the tetrahedron
Trigonal Bipyramidal	two axial positions as a set three equatorial positions as a set
Octahedral	Corners of the octahedron
Pentagonal Bipyramidal	two axial positions as a set five equatorial positions as a set

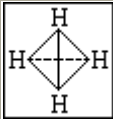
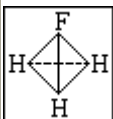
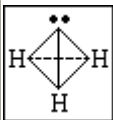
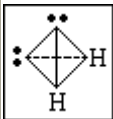
Linear Examples

H ₂	H - H	Both ends are the same. Nonpolar.
HCl	H - Cl	Both ends are not the same. Polar. Cl more electronegative than H. Polarity direction towards Cl.
CS	C [triple bond] S	Both ends are not the same. Polar. C and S have the same electronegativity. C has a -1 formal charge Polarity towards C

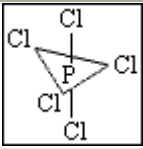
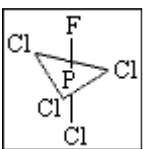
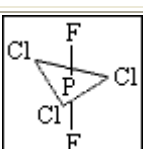
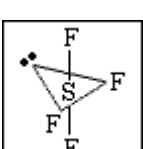
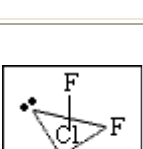
Trigonal Planar Examples

BCl ₃		all triangle corners are the same. Nonpolar.
BCl ₂ Br		all triangle corners are not the same. Polar. Cl more electronegative than Br. since there are two Cl, polarity direction towards Cl.
BClBr ₂		all triangle corners are not the same. Polar. with two Br versus one Cl, the polarity direction is expected towards the Br.
SO ₃		all triangle corners are the same. Nonpolar.
SO ₂		all triangle corners are not the same. Polar. the lone pair on the S versus two O would make a reasonable polarity direction difficult even with O more electronegative than S

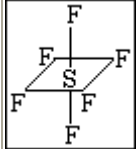
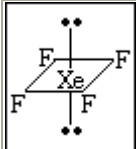
Tetrahedral Examples

CH ₄	 A diagram of a tetrahedron with a central carbon atom (implied at the center) and four hydrogen atoms (H) at the corners. The front edge is a horizontal line with H at each end. Two lines go from the center to the top and bottom vertices, and two diagonal lines connect the corners to form the back edge.	all tetrahedron corners are the same. Nonpolar.
CH ₃ F	 A diagram of a tetrahedron with a central carbon atom (implied at the center) and three hydrogen atoms (H) at the corners and one fluorine atom (F) at the top vertex.	all tetrahedron corners are not the same. Polar. Even with three H versus one F, the polarity direction would likely be toward F
NH ₃	 A diagram of a tetrahedron with a central nitrogen atom (implied at the center) and three hydrogen atoms (H) at the corners and one lone pair of electrons (represented by two dots) at the top vertex.	all tetrahedron corners are not the same. Polar. with three H versus one N, but N more electronegative than H and a N lone pair, polarity direction would be toward the lone pair
H ₂ O	 A diagram of a tetrahedron with a central oxygen atom (implied at the center) and two hydrogen atoms (H) at the corners and two lone pairs of electrons (represented by two pairs of dots) at the top vertex.	all tetrahedron corners are not the same. Polar. with two H versus one O, but O more electronegative than H and two O lone pairs, polarity direction would be toward the lone pairs

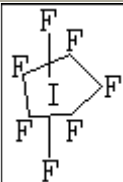
Trigonal Bipyramidal Examples

PCl_5		two axial positions are the same, and three equatorial positions are the same. Nonpolar.
PCl_4F		two axial positions are not the same. three equatorial positions are the same. Polar. Since the three equatorial positions cancel each other for polarity, the polarity direction would be toward the axial F.
PCl_3F_2		the two axial positions are the same the three equatorial positions are the same. Nonpolar.
SF_4		the two axial positions are the same the three equatorial positions are not the same. Polar. Polarity direction would be quite difficult to predict with two F versus a lone pair.
ClF_3		the two axial positions are the same the three equatorial positions are not the same. Polar. With two lone pairs versus one F, polarity direction would likely be toward the lone pairs.

Octahedral Examples

SF_6		all octahedron corners are the same. Nonpolar.
XeF_4		all octahedron corners are not the same. All opposite corners are the same; symmetry takes precedence. Thus, there is no preferred polarity direction. Nonpolar.

Pentagonal Bipyramidal Examples

IF_7		<p>The two axial positions are the same. the five equatorial positions are the same. Nonpolar.</p>
---------------	---	--

Additional Examples to Consider

N_2O	NO_2	NO_3^-	NO_2^-
I_3^-	SeF_2	PH_3	POCl_3
XeO_4	SO_3^{2-}	XeO_3	XeOF_4
XeOF_2	IF_5	TeF_5^-	IF_4^+
SF_5^+	IF_6^+	OCl_2	CO

Formal Charges

Formal charge is a way of counting electrons involved in bonding. There are some simple rules:

- 1) Any nonbonding electrons associated with an atom are counted as "belonging" to that atom.
- 2) The electrons in a bond are assigned half and half to the two atoms in the bond.

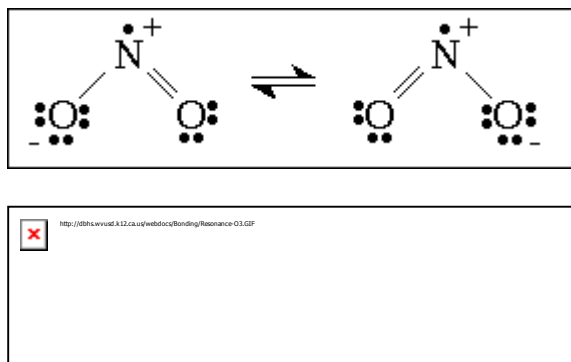
That's it for the rules. Now, how do you determine if a given atom has formal charge?

Add the two values (from above) together. Compare that to the number of valence electrons the atom has in its neutral, unbonded state.

For example, nitrogen has five electrons in its neutral state. Suppose we applied the rules to a nitrogen in a molecule and we came up with 4. That means that the formal charge on the nitrogen is +1.

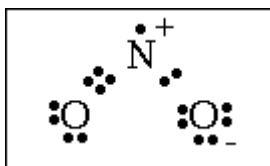
Suppose we had an oxygen and it had seven electrons associated with it. Then the oxygen would have a formal charge of -1.

Resonance structures often have formal charges associated with them. Here is NO_2 and ozone, O_3 :



In the image just below, examine the right hand oxygen. It has three nonbonding pairs, so this counts for six electrons. Then oxygen gets one of the two electrons in the bond with nitrogen. That's electron #7, giving the O a minus one formal charge.

The other O has two nonbonding pairs for 4 electrons and it also gets 2 of the four electrons in the double bond. That's six electrons, the the left hand O has no formal charge.



The nitrogen gets two electrons for the double bond, one from the single bond and one from the half-filled orbital associated with it. That's a total of 4 and gives N a +1 formal charge since it needs 5 to be neutral.

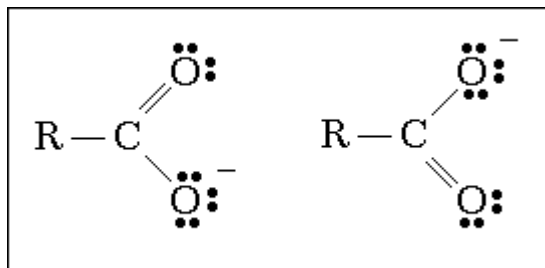
Resonance

There are a number of compounds and polyatomic ions that cannot be written using one single structure. This was known even back to the early beginnings of structural chemistry in the mid-1850s. These substances must be described in terms of "intermediate" structures, possessing non-integral bonds such as one and one-half bonds or one and one-third bonds.

Beginning in the 1920s, the first modern attempts to explain these structures started. Starting around 1930, Linus Pauling developed what today is called "resonance theory," the currently accepted way to explain the bonding in these substances. The last portion of the first sentence of "The Nature of the Chemical Bond" reads:

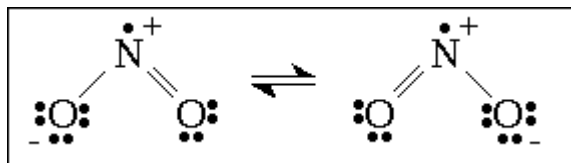
". . . we are now ready to begin the discussion of the structure of molecules to which a single valence-bond formula cannot be assigned."

The acetate anion is an example (Replace R with -CH_3 to get acetate):



Notice how the double bond can be shown attached to either oxygen. Both structures obey all the rules and there is NOTHING to rule out one structure in favor of the other.

Here is another example, using the molecule NO_2 :



Once again, note that both structures are completely within the rules.

Just one more example. Let's try the nitro-group, RNO_2^- . However, I've put the answer at the end of this document, so you could try and figure it out on your own, if you wanted to.

So. What is resonance? Resonance happens when more than one valid Lewis dot-diagram (or what Pauling calls a valence-bond structure) can be written for a molecule or ion. When this happens, the true structure is a blend of all the different possible structures.

Also, understand that the different structures contribute differently to the final structure. I will try and highlight this when I do CO and CO₂.

Now we come to some tough parts of resonance. Go back and stare at the the two NO₂ structures. Let your eye go back and forth between the two for a few seconds.

OK, here's the deal. Neither one of those two structures really does exist. The real molecule that exists in nature is a "resonance hybrid" between the two. The real molecule acts as if it had one and one-half bonds between each of the two structures. The two structures above are merely descriptive aids and, in fact, never exist.

Pauling says:

"We might say . . . that the molecule cannot be satisfactorily represented by any single valence-bond structure and abandon the effort to correlate its structure and properties with those of other molecules. By using valence-bond structures as the basis for discussion, however, with the aid of the concept of resonance, we are able to account for the properties of the molecule in terms of those of other molecules in a straightforward and simple way. It is for this practical reason that we find it convenient to speak of the resonance of molecules among several electronic structures."

OK, so you understand that the Lewis structures for NO₂, for example, don't really exist. However, there is a big misconception that some people (hey, lots of people) get. What they do is they think that the actual molecule "flips" between the two structures (or "cycles through 3 or more structures).

Like if you were to make a movie of, say, the right-side nitrogen-oxygen bond. First, it's single, then double. Then it goes back to single, then double, single, double, You get the idea. Since double bonds are shorter than singles, the O would pump in and out relative to the N. And as the right-side moves in, the left-side moves out. Back and forth, in and out. Yadda yadda yadda.

NO NO NO NO NO and I say NO NO NO NO. Let me repeat that. NO NO NO. What I just described DOES NOT happen.

The NO₂ shows two nitrogen-oxygen bonds that are stable and both consistent with being the equivalent of one and one-half bonds. The true molecule consists of only ONE arrangement of nitrogen, oxygen and electrons. NOT two.

We cannot write that structure because of the limitations of paper-and-pencil. What we do write might be called freeze-frames of the most extreme bondings in the molecule. Then we say the true molecule is some mixture of those freeze-frames.

Try and determine the resonance structures for these examples:

[ozone - O₃](#) Answer at end

[carbon monoxide - CO](#) Answer at end

[carbon dioxide - CO₂](#) Answer at end

I'm going to leave benzene - C₆H₆ - for you to discover. It is discussed in many textbooks and most probably a search on the web will bring up some good hits. There are five resonance structures considered to be important. Two of them (called the Kekulé structures) are the most important, the lesser three are collectively named the Dewar structures. By the way, benzene is the only substance I know of that has resonance structures named after people. I hope this lets you see that benzene was (and still is) a critically important compound in chemistry.

A few more, with no answers:

carbon disulfide - CS₂

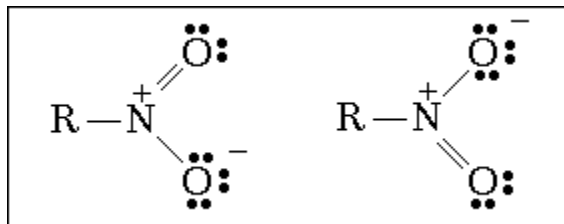
nitrous oxide - N₂O (nitrogen is the central atom)

azide ion - N₃⁻

carbon suboxide - C₃O₂ (the oxygens are at the ends of a chain)

Answers

Answer to Nitro Resonance Structures



There is a third structure possible. It has a +2 formal charge on the nitrogen and single bonds to the two oxygens. Each oxygen has three nonbonding pairs of electrons and a -1 formal charge on each.

This structure is a minor contributor to the overall structure, such that Pauling himself says " . . . with perhaps a small contribution by" when discussing this third resonance structure.

Answer to Ozone Resonance Structures

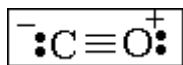


There is a third possible structure, but it is not stable and has never been shown to exist. Each of the oxygens is single-bonded to the other two oxygens, forming a triangle.

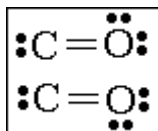
Notice how I used an equilibrium-type arrow between the two structures. Some people misinterpret this to mean the actual molecule shifts back and forth between the two structures.

IT DOES NOT!!!!!!

Answer to Carbon Monoxide Resonance Structures

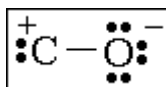


This structure just above is the classic answer given when students are asked to draw the Lewis dot-diagram for CO. However, there are three more.



This is an interesting resonance that is not discussed in the main resonance page. In these two forms, the pi bond has been rotated 90°. Let us say that one structure has the pi bond in the xy plane. Rotate it into the xz plane. That's the second resonance structure.

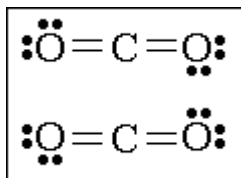
So, now we go to the last resonance structure.



Pauling identifies the percentage contribution of each structure as:

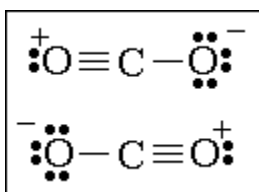
structure	% contrib.
triple bonded	
both double bonded	40
single bonded	10

Answer to Carbon Dioxide Resonance Structures



This structure just above is the classic answer given when students are asked to draw the Lewis dot-diagram for CO₂. However, there is an interesting resonance that is not discussed in the main resonance page. In these two forms, the pi bonds are at 90° to each other. Let us say that one structure has the left-hand pi bond in the xy plane. The the right-hand pi would be in the xz plane. The second resonance structure would reverse the orientation of the two pi bonds.

Here are the other two resonance structures:



Pauling identifies the percentage contribution of each structure to the actual "resonance hybrid" as 25% each.